EVAPORATION KINETICS OF InSb

by

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Introduction

In the slow vacuum evaporation of binary alloys, of which indium antimonide is one, a preferential evaporation of the more volatile component of the two occurs, inviting the production of layers of indium, antimony and indium antimonide, rather than the deposit of a homogeneous film of indium antimonide. Methods of preventing such preferential evaporation, so as to produce homogeneous films, have been studied extensively. Two methods are commonly used:

1. "Flash" evaporation technique: the alloy is explosively evaporated by dropping finely divided particles onto the hot surface of the furnace in the vacuum system.

2. Evaporation from a multiple source: the two components of the binary alloy are evaporated simultaneously from separate crucibles, the temperature of each being adjusted so that the evaporation gives a stoichiometric deposit of film.

The first method is not very useful when slow deposition rates are required, as for example, in the growth of single crystal evaporated films. The second method requires inconveniently close control of the crucible temperatures.

Other methods of controlling film composition involving control of the liquid composition may be conceived. These require a knowledge of the evaporation characteristics of In-Sb mixtures.

Theory. Raoult's[1] Law states that the vapor pressure of a dilute solution is lower than that of the pure solvent by an amount proportional to the concentration of the solute, i.e.,

$$\frac{P_V - P_S}{P_V} = X_L = \frac{N_L}{N_L + N_V} \qquad (1)$$

where P_S is the vapor pressure of the solution: P_V is that of the pure solvent; X_L is the mol-fraction of the solute present in the solution; N_L and N_V are the numbers of mols of solute and solvent respectively.

Equation (1) gives

$$1 - X_L = X_V = \frac{N_V}{N_L + N_V} = \frac{P_S}{P_V} \tag{2}$$

Dushman[2] applied Raoult's law to binary alloys. By treating each component in turn as a solvent, he obtained the result that the depression of the vapor pressure in the solution, $P_1 - P_A$, is proportional to the concentration of the solute, i.e.,

$$\frac{P_1 - P_A}{P_1} = 1 - X_A$$

$$\frac{P_A}{P_1} = X_A \tag{3a}$$

and

$$\frac{P_2 - P_B}{P_2} = 1 - X_B$$

$$\frac{P_B}{P_2} = X_B \tag{3b}$$

where P_A and P_B are the respective partial vapor pressure of the components A and B in the binary alloy, P_1 and P_2 the respective vapor pressure of the pure substances A and B, and X_A and X_B the mol fractions of the components A and B respectively.

P_A and P_B can be determined experimentally, but the procedure is extremely difficult and involved, and no ready information is available, while P_1 and P_2 can be obtained at a given temperature T^oK from the equation by Dushman[2]:

$$\text{Log } P = A - \frac{B}{T} \tag{4}$$

where A and B are constants deduced by Dushman,[2] and P the vapor pressure of the pure substance.

The Langmuir[3] equation for the mass evaporated per unit emitting area per unit time is given as:

$$E = kP\sqrt{\frac{M}{T}} \tag{5}$$

where M is the molecular weight of the substance evaporated, P its vapor pressure at temperature $T^{o}K$ and k a constant. Therefore, in an alloy, assuming no preferential evaporation, the ratio of the rate of evaporation of the two components, in terms of equation (5), is given by

$$\frac{E_A}{E_B} = \frac{P_A}{P_B}\sqrt{\frac{M_A}{M_B}} \tag{6}$$

substituting equation (3a) and (3b), equation (6) gives

$$\frac{E_A}{E_B} = \frac{X_A P_1}{X_B P_2}\sqrt{\frac{M_A}{M_B}} \tag{7}$$

If W_A and W_B represent the concentration # by weight of the components A and B in the liquid respectively, then

$$\frac{W_A}{W_B} = \frac{X_A M_A}{X_B M_B} \text{ or } \frac{X_A}{X_B} = \frac{W_A M_B}{W_B M_A} \tag{8}$$

Equation (7) then gives

$$\frac{E_A}{E_B} = \frac{W_A P_1}{W_B P_2}\sqrt{\frac{M_B}{M_A}} \tag{9}$$

For evaporation without component separation, $\frac{E_A}{E_B}$ must be equal to $\frac{W_A}{W_B}$, meaning $\frac{P_1}{P_2}\sqrt{\frac{M_B}{M_A}}$ should be unity.

The calculation of the vapor pressure of pure indium and antimony, P_{In} and P_{Sb}, at a temperature of $1200^{o}C$, using equation (4) gives

P_{In} - - - - - - - - - 4.8×10^{-1} mm of Hg.

P_{Sb} - - - - - - - - - 49.0 mm of Hg.

Antimony by itself evaporates largely in the form of molecules Sb_2, so the molecular weight used in the estimation was M = 2 x 121.8 = 243.6. The ratio $\frac{P_1}{P_2}\sqrt{\frac{M_B}{M_A}}$ is found to be approximately 70 using the above values of P_{Sb} and P_{In} as the pressures P_1 and P_2 respectively and the molecular weights of antimony and indium for M_B and M_A. That is, antimony evaporates about 70 times faster than indium, for the same concentration in the liquid and the same temperature.

In practice, the validity of using Raoult's Law for the InSb system is questionable, because it is not certain that liquid In-Sb alloys behave as ideal solutions. Also, there is a general lack of agreement in the published vapor pressures of pure substances. Moreover, evaporations of InSb are usually made from a stationary charge in an open crucible. Since the surface area of the evaporant is of the same order of magnitude as the opening of the crucible, the rate of molecular effusion cannot be accurately determined by the Langmuir equation, which is derived with the assumption of equilibrium conditions. Many other factors may also cause the evaporation characteristics of indium antimonide to deviate from the theoretical determination applying Raoult's Law and the Langmuir equation. But the method of producing thin films of InSb by vacuum evaporation in an open crucible is so widely practiced that the information of the characteristics of its evaporation under such conditions is useful. The purpose of the following experiment is to determine the evaporation characteristics of InSb experimentally.

EXPERIMENTAL PROCEDURE

Crucible charges of InSb or antimony-rich InSb were evaporated from an open crucible in a vacuum system. The composition of the vapor above the crucible of In-Sb mixture was determined for various temperatures, and for

various concentrations of the constituents by condensing the vapor on carbon spectographic electrode, and analysing the deposits spectrographically.

Calibration. Samples of indium and antimony were carefully weighed and transferred to the carbon crucible in the vacuum system, as shown in Fig. 1, Plate 1. Four graphite spectrographic electrodes were mounted on the holder fixed above the crucible. The system was pumped down to a pressure of about 4×10^{-5} mm of mercury. Evaporation onto the electrodes was made at a temperature of about $1200^{\circ}C$. Care was taken to be certain that all of the sample was completely evaporated before the electrodes were dismounted from the substrate holder for the later analysis.

Analysis. The analytical samples of InSb and antimony-rich InSb were evaporated in the same vacuum system but with a different substrate holder, as shown in Fig. 2, Plate 1. Eight electrodes were mounted in a circle near the edge of a disc that could be rotated from outside the system through a rotary seal. A shield was also used with an opening so that one substrate at a time was exposed to the evaporating In-Sb mixture. The opening was placed at the same distance from the crucible as the substrates previously used for the working curves. A tublar loader was mounted beside the crucible. The purpose fo the loader was to accommodate the sample to be evaporated before the crucible reached the required temperature. When the temperature was reached, the sample was dumped into the crucible by tilting the loader with the magnet.

Before the evaporation, the weighed sample of InSb or antimony-rich InSb were put in the crucible to be melted into spherical shape for easy delivery from the loader to the crucible in the evaporation afterwards.

During each evaporation, one substrate (electrode) after another was rotated into place above the crucible, the various evaporation times being

regulated by trial and error so that a measurable amount of In and/or Sb was deposited on each substrate and so that no evaporant remained in the crucible after the final evaporation. Again great care was taken in dismounting the substrates.

Analytic Method. The indium and/or antimony deposits collected by the graphite electrodes were in very small quantities, of the order of a few microgram. To assure reasonable accuracy, suitable analytic procedures are required.

Much work has been done by professional spectrochemists on the detection of impurities in metals, where the constituents to be detected are small fractions of the whole sample being analysed. The accuracy for such analyses usually is in the range of 2 to 7 per cent of the amount present. Experience shows that for analysis of constituents amounting to as much as 13% of the total sample ordinary spectroscopic methods are highly unreliable. Since this experiment requires the analysis of the entire range of concentrations of indium and antimony in InSb, i.e. the detection from 0 up to 100 per cent, the conventional procedure using an internal standard is not very suitable. The reasons that an internal standard cannot be used in the present case are as follows:

(1) The internal standard should have a negligibly small concentration in the analysis specimens, and an amount smaller than the thin film of InSb on the graphite electrode would be too small to measure accurately.

(2) No single internal standard element has the similarity in the rate of volatization, excitation potential and self-absorption as both indium and antimony.

(3) The internal standard method cannot give the information of the absolute amount of the substance evaporated, which is essential in this experiment.

PLATE I

Fig. 1 Arrangement of the vacuum system for the working curves.

Fig. 2 Arrangement of the vacuum system for the analysis.

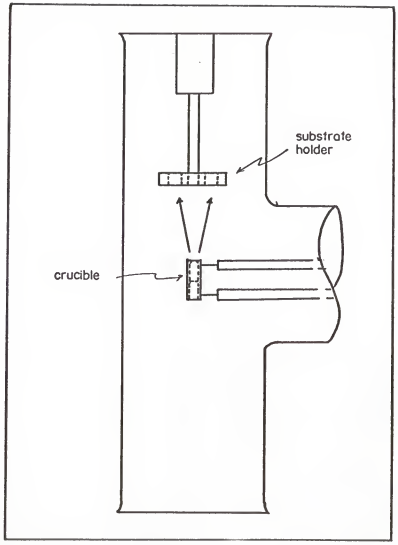

Fig. 1

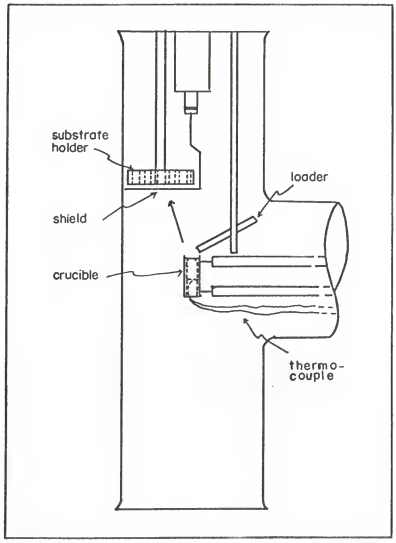

Fig. 2

PLATE I

With no addition of internal standard, the electrodes, after taken down from the substrate holder, were arced, one by one, in a 150-volt d-c. arc source. The spectrograph used for the analysis was a Bausch and Lomb's large quartz spectrograph of the Littrow type. An adjustable step-sector was used to cut the light intensity down by a factor of 13/16, so that the spectral intensities of the selected lines were within the workable range of the emulsion-characteristic curve. Since the microphotometer records only the percentage transmission of the image of the spectral lines on the spectrum analysis plate, this characteristic curve is necessary to convert the percentage transmission of the lines back to their spectral intensity. Known intensity variation was calibrated by a step-sector of geometric ratio 1·5, rotating above a critical frequency to escape intermittency effect and reciprocity-law failure[6]. Each spectral line then varied in intensity from one end to the other in discrete steps of the geometric ratio of the step-sector. The percentage transmission of the various segments of the line was measured by the microphotometer.

To provide a smooth emulsion-characteristic curve of the entire workable intensity range, a "high-low" curve[5] was used. A "high" reading on this curve is the percentage transmission reading of any one segment of a spectral line and a "low" reading is the percentage transmission reading of its adjacent segment. The latter corresponds to an exposure 1·5 times lower than that of the high reading since the exposure from adjacent steps of the step-sector differ by a factor of 1·5. Six lines in all were used and their percentage transmissions of the various segments tabulated in Table 1. The "high-low" curve was plotted with the "high" reading as the ordinate and the "low" reading the abscissa, as shown in Plate II.

From the "high-low" curve, smoothed values of "high" readings were chosen, and their corresponding "low" readings obtained. A table was set up

PLATE II

A "high-low" curve with "High" reading plotted against "Low" reading.

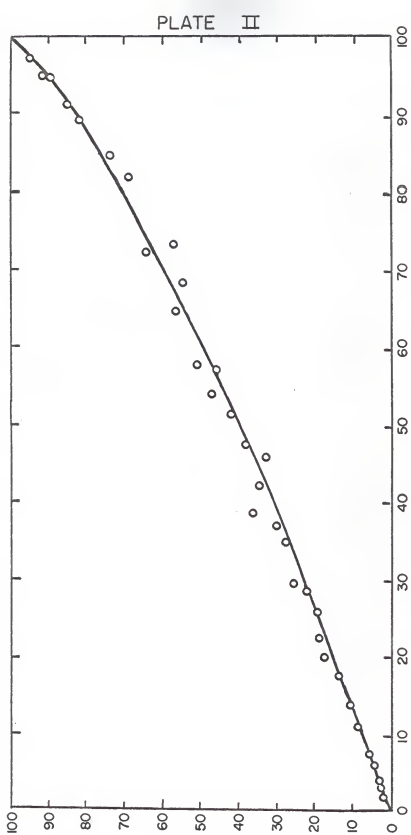
PLATE II
HIGH READING
LOW READING
0
10
20
30
40
50
60
70
80
90
100

Table 1

Geometric ratio of the step-sector used: 1·5
Number of steps: 7

Lines for Calibration	Percentage transmission for: Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7
In - 3256	1.75	2.24	2.96	4.24	5.98	7.46	10.50
In - 3039	8.45	10.95	13.95	17.45	19.95	22.45	28.90
In - 2933	18.90	26.10	29.70	37.00	38.50	47.30	53.80
In Unidentified I	27.90	34.90	42.30	51.60	57.50	64.70	72.60
In Unidentified II	31.70	46.20	56.80	73.60	85.10	91.50	95.00
In Unidentified III	53.80	68.50	82.00	89.50	95.20	97.20	---

with these readings, as shown in Table 2, such that each succeeding reading corresponds to a spectral intensity 1·5 times higher than the previous one (Intensity is proportional to exposure since E = It and t is constant). Since the intensity depends fundamentally on the position of the zero of the intensity scale, the first percentage transmission reading in Table 2 was chosen to have unit intensity. This makes the intensity of the succeeding reading 1·5 and the one following $(1{\cdot}5)^2$ and so on. Since the intensity steps used

Table 2

Percentage Transmission	Log 1·5 I	Percentage Transmission	Log 1·5 I
99.00	0	28.25	10
97.50	1	22.25	11
94.50	2	17.25	12
89.25	3	13.25	13
81.50	4	10.00	14
72.25	5	7.50	15
62.50	6	6.25	16
52.75	7	4.25	17
43.75	8	3.00	18
35.50	9	2.25	19

PLATE III

The emulsion-characteristic curve with %T plotted against $\log_{1.5}$ Intensity.

PLATE III

100
90
80
70
60
50
40
30
20
10
0
% T
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
LOG1.5 I

have a simple integral ratio 1·5, the log I values to this base are successive integers. From the data of Table 2, the tabulated percentage transmission readings were plotted against these $\log_{1.5}$ values on ordinary co-ordinate paper and an emulsion-characteristic curve was constructed, as shown in Plate III.

The complete processing of the spectrum analysis plate for the emulsion-characteristic curve, as well as for the rest of the experiment, is consistently as follows:

Developer (Eastman Formula D19)	3 min. 30 sec.
Rinse and transfer	10 sec.
Fix (Eastman Acid Fixer F-15)	10 min.
Wash	60 min.
Total time	73 min. 40 sec.

With the emulsion-characteristic curve provided, the evaporated films of indium and/or antimony for the working curves and the analysis were arced, the plates developed and measured and the spectral intensities were then determined from the curve, with the percentage transmission known.

Working Curves.[1] Two spectral lines, In-2932 and In-2753, were chosen for indium and one, Sb-2877, for antimony. Working curves for these lines, shown in Plate IV and Plate V, were constructed by plotting log intensity against log concentration from the data shown in Table 3 and Table 4.

EXPERIMENTAL RESULTS

The evaporations of the analysis samples of InSb and antimony-rich InSb were made at temperatures from 800°C to 1100°C. For the evaporation of InSb at 800°C, no trace of indium was present after evaporating for several hours. Six samples, three of pure InSb and three of antimony-rich InSb, were prepared and evaporated at temperatures above 800°C. The concentrations by weight of the evaporated films on the electrodes were measured from the working curves, and together with the evaporation time for each

PLATE IV

The working curves of indium with log I plotted against log conc. of In in milligram.

Spectral line I : In-2753

Spectral line II: In-2932

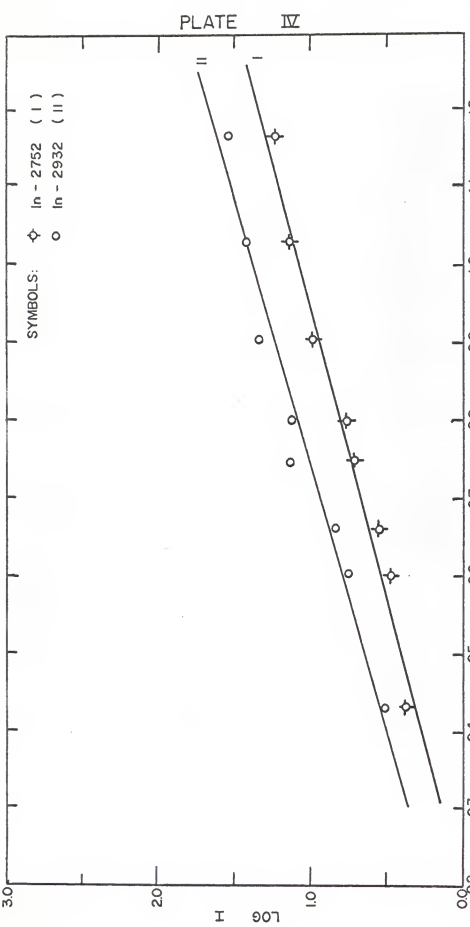
PLATE IV
SYMBOLS:
In - 2752 (I)
In - 2932 (II)
LOG I
LOG CONC. OF In IN MG
0.0
1.0
2.0
3.0
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
II
I

PLATE V

The working curve of antimony with log I plotted against log conc. of Sb in milligram.

Spectral line: Sb-2877

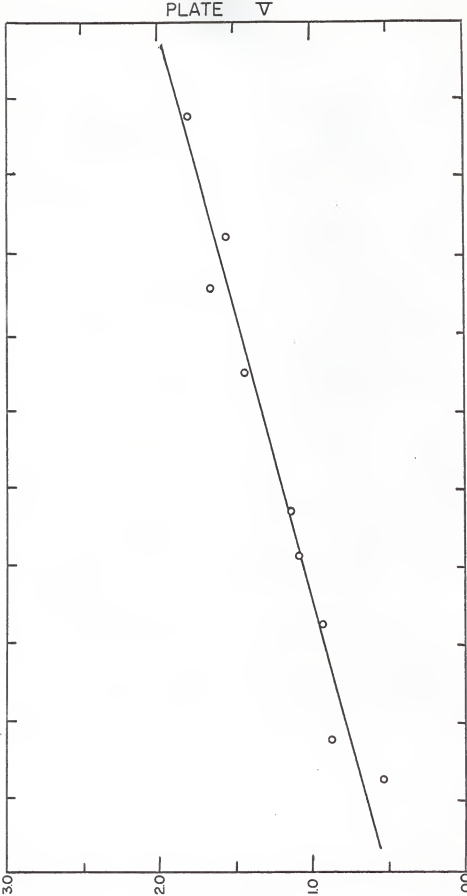
PLATE V
LOG I
3.0
2.0
1.0
0.0
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
LOG CONC. OF Sb IN MG

Table 3

Spectral lines used:
I = In-2753
II = In-2932

Wt. of In (mg)	log In	Percentage Transmission	log 1
14.60	1.1644	I 53.6	1.223
		II 37.4	1.544
10.75	1.0315	I 57.1	1.154
		II 43.6	1.427
8.00	.9031	I 65.1	1.007
		II 46.6	1.357
6.30	.7993	I 78.4	0.766
		II 57.7	1.144
5.60	.7482	I 79.9	0.733
		II 56.8	1.162
4.60	.6628	I 88.3	0.546
		II 74.2	0.834
4.00	.6021	I 90.9	0.463
		II 78.8	0.757
2.70	.4314	I 93.8	0.370
		II 98.5	0.511

Table 4

Spectral line used: Sb-2877

Wt. of Sb (mg)	log Sb	Percentage Transmission	log I
14.85	1.1718	10.0	2.467
11.90	1.1315	16.6	2.140
9.60	.9823	18.3	2.070
7.80	.8921	23.0	1.910
6.80	.8325	24.3	1.866
4.5	.6532	37.7	1.541
3.5	.5441	47.8	1.330
3.00	.4771	41.7	1.452
2.10	.3222	54.4	1.208

film, the data are tabulated in Table 5. The total concentration of indium and antimony measured from the working curves was found to be consistently 64% ± 1% and 71% ± 7% respectively of the previously weighed samples, except for two pure InSb samples, which were evaporated several weeks after the other samples. It was assumed that this discrepancy was caused by the slight varying of pressure in the vacuum system during the sample evaporations.

Consequently all concentrations have been scaled to 100% of the total samples, as tabulated in Table 6.

The results of the experiment are summarized in Plate VI and VII. The values of the mol-fraction of antimony vapor, X_{Sb}, and indium vapor, X_{In}, were plotted against the concentrations of antimony and indium in the crucible, as shown in Fig. 1 and Fig. 2 of Plate VI for a pure InSb initial crucible charge and Fig. 1 and Fig. 2 of Plate VII for an antimony-rich InSb initial crucible charge. The concentrations of antimony and indium in the crucible corresponding to a given vapor sample were obtained by subtracting from the known crucible charge the sum of the amounts in the vapor samples previously collected from the same crucible charge. Thus $(X_{n,Sb})$ crucible = $(X_{Total,Sb})$ crucible - $\sum_{i=1}^{n-1} (X_{n,Sb})$ vapor, and likewise for indium. The vapor concentrations were adjusted, of course, so that the sum of the vapor concentrations was equal to the original crucible charge.

DISCUSSION

The nature of these characteristic curves of evaporation follows more or less a consistent pattern, even at different temperatures and concentrations. The high concentration of the antimony vapor at the beginning of the evaporation indicates that preferential evaporation of antimony does occur, as would be expected. Nevertheless, the ratio of the rates of evaporation of antimony and indium cannot be quantitatively estimated by equation (9) with vapor pressure values derived from tables compiled by Dushman[2]. Experimental results show that all the values of E_{Sb}/E_{In} (obtained from Table 6 by dividing column 2 by column 3, which are the concentrations of the antimony and indium vapor respectively emitting from the same area of surface for the same period of time) are never more than 16 at the beginning of the evaporation and are

Table 5

Sample No.	Initial Concentration (mg)	Electron No.	1	2	3	4	5	6	7	8
E	InSb 95.9 + Sb 17.8	t°c:	906°C	906°C	906°C	906°C	906°C	906°C	906°C	906°C
		Conc. In of (mg)	1.80	3.18	4.32	4.60	3.73	2.46	3.41	3.18
		Vapor Sb	17.70	11.61	3.66	2.97	2.50	1.78	3.13	4.85
		Time:	5 min.	10 min.	10 min.	15 min.	15 min.	20 mn.	20 min.	30 min.
L	InSb 102.1 + Sb 26.7	t°c:	1000°C	1000°C	1006°C	1012°C	1006°C	1000°C		
		Conc. In of (mg):	1.00	3.63	5.96	12.16	3.47	5.09		
		Vapor Sb	17.80	10.07	7.62	12.34	4.32	4.27		
		Time:	1 min.	2 min.	4 min.	7 min.	7 min.	10 min.		
N	InSb 119.5 + Sb 32.0	t°c:	1094°C	1094°C	1094°C	1094°C	1090°C	1090°C		
		Conc. In Of (mg):	2.50	2.24	8.17	14.35	6.61	3.37		
		Vapor Sb	16.30	13.58	12.97	12.91	9.06	4.32		
		Time:	30 sec.	50 sec.	1 m,40s.	3 min.	4 min.	4 min.		
Q	InSb 109.4	t°c:	908°C	908°C	905°C	908°C	914°C	915°C		
		Conc. In of (mg):	2.41	10.17	8.22	6.27	3.43	2.93		
		Vapor Sb	20.18	7.55	5.56	3.04	2.55	1.30		
		Time:	3 min.	15 min.	15 min.	20 min.	20 min.	30 min.		
R	InSb 108.9	t°c:	1010°C	1012°C	1018°C	1016°C	1016°C	1016°C		
		Conc. In of (mg):	.60	4.09	11.04	6.67	4.17	.80		
		Vapor Sb	9.66	6.64	5.41	2.19	2.75	.60		
		Time:	12 sec.	1 min.	4 min.	5 min.	7 min.	10 min.		
S	InSb 108.4	t°c:	956°C	956°C	956°C	956°C	956°C	956°C		
		Conc. In of (mg):	.30	.30	2.02	3.47	6.61	7.76	4.32	3.20
		Vapor Sb	2.08	2.94	4.98	3.71	4.61	4.18	6.53	2.71
		Time:	10 sec.	20 sec.	1 min.	2 min.	4 min.	10 min.	20 min.	20 min.

Table 6

Comesp. electrode No.	Conc. of Sb vapor(mg)	Conc. of In vapor(mg)	X_{Sb} of vapor	X_{In} of vapor	Amount of Sb in crucible	Amount of In in crucible	Total amount of evaporant in crucible
E							
1	25.00	2.82	.895	.105	73.58	45.72	119.30
2	16.28	4.97	.760	.240	48.58	42.90	91.48
3	5.13	6.75	.415	.585	32.30	37.93	70.23
4	4.16	7.20	.355	.645	27.17	31.18	58.35
5	3.50	5.83	.365	.635	23.01	23.98	46.99
6	2.50	3.58	.395	.605	19.51	18.15	37.66
7	4.38	5.33	.435	.565	17.01	14.57	31.58
8	6.80	4.97	.565	.435	12.63	9.24	21.87
residue	5.83	4.27	.565	.435	5.83	4.27	10.10
L							
1	25.10	1.56	.935	.075	79.20	48.96	128.16
2	14.10	5.68	.700	.300	54.10	47.40	101.50
3	10.66	9.33	.515	.485	40.00	41.72	81.72
4	17.30	19.00	.465	.535	29.34	32.39	61.73
5	6.06	5.43	.515	.485	12.04	13.39	25.43
6	5.98	7.96	.415	.585	5.98	7.96	13.95
N							
1	23.00	3.36	.860	.140	96.99	57.69	152.68
2	19.01	3.51	.830	.170	73.99	54.33	128.32
3	18.15	12.78	.575	.425	54.98	50.82	105.80
4	18.09	22.45	.435	.565	36.83	38.04	74.87
5	12.68	10.33	.535	.465	18.74	15.59	34.33
6	6.06	5.26	.525	.475	6.06	5.26	11.32
Q							
1	28.30	3.77	.790	.210	56.30	52.26	108.56
2	10.57	15.90	.385	.615	28.00	48.49	76.49
3	7.78	12.85	.365	.635	17.43	32.59	50.02
4	4.26	9.80	.290	.710	9.65	19.74	29.39
5	3.57	5.36	.385	.615	5.39	9.94	15.33
6	1.82	4.58	.270	.730	1.82	4.58	6.40

Table 6

(Continued)

Corresp. electrode No.	Conc. of Sb vapor(mg)	Conc. of In vapor(mg)	X_{Sb} of vapor	X_{In} of vapor	Amount of Sb in crucible	Amount of In in crucible	Total Amount of evaporant in crucible
S							
1	3.96	.57	.860	.140	60.31	53.19	113.50
2	5.58	.57	.905	.095	56.35	52.62	108.97
3	9.46	3.84	.700	.300	50.77	52.05	102.83
4	7.05	6.60	.505	.495	41.31	48.21	89.52
5	8.76	12.87	.395	.605	34.26	41.61	75.87
6	7.95	14.75	.335	.665	25.50	29.04	54.54
7	12.40	8.21	.585	.415	17.55	14.29	31.84
8	5.15	6.08	.445	.555	5.15	6.08	11.23
R							
1	18.35	1.14	.935	.065	51.76	52.88	104.64
2	12.60	7.79	.585	.415	33.41	51.74	85.15
3	10.28	21.67	.310	.690	20.81	43.95	64.76
4	4.16	12.83	.230	.770	10.53	22.28	32.87
5	5.23	7.93	.385	.615	6.37	9.45	15.82
6	1.14	1.52	.415	.585	1.14	1.52	2.66

PLATE VI

Fig. 1 The mol-fraction of Sb vapor plotted against the instantaneous amount of antimony in the crucible for pure InSb crucible charge.

Fig. 2 The mol-fraction of In vapor plotted against the instantaneous amount of indium in the crucible for pure InSb crucible charge.

Fig. 3 The mol-fraction of Sb vapor and In vapor plotted against the instantaneous total amount of evaporant in the crucible for pure InSb crucible charge.

PLATE VI

FIG 1

FIG 2

FIG 3

PLATE VII

Fig. 1 The mol-fraction of Sb vapor plotted against the instantaneous amount of antimony in the crucible for antimony-rich InSb crucible charge.

Fig. 2 The mol-fraction of In vapor plotted against the instantaneous amount of indium in the crucible for antimony-rich InSb crucible charge.

Fig. 3 The mol-fractions of Sb vapor and In vapor plotted against the instantaneous total amount of evaporant in the crucible for antimony-rich InSb crucible charge.

PLATE VII

FIG 1

FIG 2

FIG 3

quite close to unity later in the evaporation for the given temperatures. The values as calculated from equations (4) and (9) in the theory, using the constants given by Dushman[2], are at least 6 times the experimental values. This discrepancy possibly can be explained from the fact that the diffusion of antimony from within the sample to the evaporating surface, at the beginning of the evaporation when the antimony was evaporating at a very fast rate, could not readily maintain its concentration at the surface, thus increasing the effective concentration of indium and thus its rate of evaporation, as mentioned previously.

Later in the evaporation, a relatively more constant rate of evaporation was attained, as evidenced from the flat portion of the curves shown in Plate VI and Plate VII. Both pure InSb samples and antimony-rich InSb samples have a higher mol-fraction of indium vapor than of antimony in this region. However, the flat portion of the curves for initially antimony-rich crucible charge lies closer to the equal concentrations of antimony and indium vapor (ie. $X_{In} = X_{Sb} = \frac{1}{2}$) than that for pure InSb crucible charges. This suggests that diffusion of antimony through the surface is, in fact, an important effect. Another difference was found in the composition of the evaporant from the pure InSb charge and the antimony-rich InSb charge, when they were evaporating equal concentrations of antimony and indium vapor. For every sample of pure InSb, the evaporant was found to be richer in indium, while for every antimony-rich sample, the composition in the crucible, as in the vapor, was of nearly equal concentrations of indium and antimony. For example, in the case of Sample R, for which the starting material in the crucible was pure InSb, when the sample was evaporating equal vapor concentration of indium and antimony, the evaporant left in the crucible had a concentration of 30 milligram of antimony and 51 milligram of indium. For the same

evaporation temperature 1000°C, in the case of Sample L, where the initial charge was antimony-rich InSb, the evaporant has a concentration of 39 milligrams of antimony and 40 milligram of indium when evaporating equal vapor concentration of indium and antimony.

SUMMARY

Preferential evaporation of antimony does occur at the beginning of the evaporation of InSb in open crucibles commonly used. However, the ratio of the evaporation rates of antimony and indium cannot be estimated with precision by methods recommended by Holland[3] for binary alloys. Following the initial preferential evaporation of antimony, a fairly constant rate of evaporation takes place of slightly higher concentration of indium vapor. This suggests that at the start of evaporation of InSb, antimony would evaporate faster, being more volatile, but as evaporation goes on both antimony and indium vapors come off at a fairly constant rate, and later with higher concentration of indium vapor. The evaporation characteristics deduced from this experiment agree with that of Kurov and Pinsker[4].

Future Study

The author suggests more intense studies on the constant-rate evaporation of binary alloys. If the constant rate is attained when the vapors are of equal concentration, the tedious multi-sources method can be eliminated in the production of stoichiometric alloy films.

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EVAPORATION KINETICS
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The vacuum evaporation of InSb from a crucible containing equal proportions of indium and antimony invites the preferential evaporation of antimony. Applying Dushman's law for binary alloys, calculations show that antimony would evaporate about 70 times faster than indium at 1200°C and that the ratio is even larger at lower temperatures. Since the use of Dushman's theory requires many assumptions, an experimental survey is essential.

Charges of In-Sb mixture were evaporated from an open crucible in a vacuum system for temperatures ranging from 800°C to 1100°C and for various concentrations of the constituents. As the evaporation proceeded, the vapor above the crucible was deposited into eight graphite spectrographic electrodes, one at a time. The time of exposure of each substrate was regulated so that each received a measureable quantity. The deposits on the electrodes were then analysed spectrographically. From the data, the values of the mol-fractions of antimony vapor and indium vapor were determined simultaneously with the instantaneous concentrations of antimony and indium in the crucible and the instantaneous total amount of the evaporant in the crucible. For the evaporation at 800°C, no trace of indium was found in the vapor. For temperatures above 800°C up to 1100°C, the evaporation characteristic curves tended towards a pattern: Initially the relative concentration of the antimony vapor and the total evaporation rates were high. As the evaporation proceeded, the evaporation rate decreased, and the vapor composition became nearly constant with a slight excess of indium.

From these evidences, conclusions are drawn that preferential evaporation of antimony does occur at the beginning of the evaporation, though the results show that the experimental value of the ratio of the rates of evaporation of antimony and indium for open crucible is 1/6 of that calculated previously applying Dushman's law for binary alloys. However, no preferential evaporation

of antimony is shown later in the evaporation. A possible explanation of this behavior is that the diffusion of antimony from within the evaporant does not proceed rapidly enough to maintain its surface concentration, thus favoring the evaporation of indium.

It is inferred that if the constant rate of evaporation of InSb can be controlled, the vacuum deposition of In-Sb mixtures offers a simple and efficient method for the production of stoichiometric InSb films.